

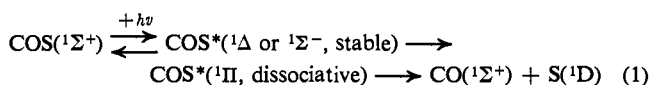
Direct Photolysis of Carbonyl Sulfide in Solution. Reactions of Singlet D Sulfur Atoms in the Liquid Phase

Eberhard Leppin and Klaus Gollnick

Contribution from the Max Planck Institut für Kohlenforschung,
Abteilung Strahlenchemie, Mülheim/Ruhr, Germany. Received October 7, 1969

Abstract: Photolysis of COS at 2537 Å and 25° in various alkanes gives rise to the formation of CO, elemental sulfur, and mixtures of the corresponding isomeric mercaptans produced by S(¹D) "insertion" reactions into the different C-H bonds present in a particular saturated hydrocarbon. In contrast to gas-phase reactions, S(¹D) atoms in solution insert selectively. The rates of insertion increase in the order primary < secondary < tertiary C-H bonds. The different behavior of S(¹D) atoms in the two phases is explained by assuming that nonthermalized sulfur atoms are involved in the gas-phase reactions, whereas thermalized sulfur atoms react in the liquid phase. The stereospecificity of S(¹D) insertions as occurring with retention of configuration was shown with *trans*- and *cis*-1,4-dimethylcyclohexane as well as with *trans*- and *cis*-1,2-dimethylcyclopropane. Mechanistically, S(¹D) insertion is considered as taking place *via* an initial attack of S(¹D) atoms on the H atoms rather than on the C-H bond (three-center mechanism), thus forming transition states in which the radicals are H-bonded, followed by rotation of the radical pair into favorable positions for C-S bond formation before separation can occur. This view is supported by the fact that the rates of insertion parallel the frontier electron densities at the particular H atoms involved. S(¹D) → S(³P) transitions are catalyzed by alkanes, alcohols, and aromatic hydrocarbons such as cyclohexane, ethyl alcohol, and benzene in relative rate ratios of 1:7:200. It is proposed that EDA complexes of solvent molecules (as electron donors) and S(¹D) atoms (as electron acceptors) are involved in the singlet D sulfur to triplet P sulfur quenching processes.

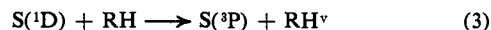
When carbonyl sulfide is photolyzed in solution at 2537 Å, sulfur atoms in their singlet D state are produced according to



with a quantum yield of 0.9, independent of the nature of the solvent used.¹ In alkanes, S(¹D) atoms give rise to the formation of mercaptans



as well as of triplet P sulfur atoms in a solvent-catalyzed process



(where RH^ν = vibrationally excited ground-state solvent molecules), whereas in methanol, ethyl alcohol, and acetonitrile only reaction 3 is observed.¹ Triplet P sulfur atoms seem to be incapable of reacting with C-H bonds in solution¹ and in the gas phase at room temperature,² but may recombine in solution to S₂ molecules which, as was shown for the gas phase,² polymerize to elemental sulfur.

The present paper reports on the selectivity and stereospecificity of S(¹D) atom reactions with various alkanes and on the efficiency of various solvents in catalyzing the singlet-to-triplet transition of sulfur atoms.

Experimental Section

COS was purchased from Matheson Company. Hydrocarbons were Phillips Petroleum Company pure grade and Fluka Purum. Purification of COS, alkanes, and other solvents is described elsewhere.¹ In some experiments, COS was used without purification after it was checked that products and product distributions remained unaltered in comparison with experiments carried out with

purified COS. Irradiation and work-up procedures were followed as described in the preceding paper.¹

Qualitative and quantitative analysis of the mercaptans formed was achieved gas chromatographically using Perkin-Elmer fractometers F-6 and F-20 (Bodenseewerk) and capillary columns 1-G-26 (50 m, phenylsilicone oil DC 550) and 1-G-50 (50 m, di-*n*-decyl phthalate + trimer acid). Because of the small conversions during one run (≤0.5% of the starting amounts of COS) and the resulting minute amounts of reaction products, the starting material was removed by low-temperature distillation before analyzing the products. A full account of the method of gas chromatographic identification of isomeric mercaptans produced from alkanes containing different C-H bonds has appeared elsewhere.³ Relative amounts of isomeric mercaptans were determined from vpc peak areas assuming that, using a flame ionization detector, the response factors are approximately the same for isomeric mercaptans having more than four carbon atoms (*cf.* ref 4).

CO quantum yields were determined according to the procedure already described.¹

Results and Discussion

(a) Selectivity of Singlet D Sulfur Atom "Insertion" Reactions. Product Distributions and Relative Rates

Photolysis of COS at 2537 Å and 25° in *n*-pentane, isopentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane, and methylcyclohexane results in the formation of carbon monoxide,⁵ elemental sulfur, and mixtures of the corresponding isomeric mercaptans. H₂S, H₂S₂, and other products expected from reactions of free alkyl radicals could not be detected in the low-conversion runs in which less than 0.5% of the COS present in saturated solutions was photolyzed.

The individual mercaptans of such reaction mixtures were identified gas chromatographically.³ Primary, secondary, and tertiary mercaptans are easily distin-

(3) E. Leppin, K. Gollnick, and G. Schomburg, *Chromatographia*, **2**, 535 (1969).

(4) R. Kaiser, "Chromatographie in der Gasphase," Vol. 3, Bibliographisches Institut, Mannheim, Germany, 1962.

(5) The quantum yield of CO formation was determined for COS photolysis in *n*-pentane and found to be 0.90 ± 0.05 in agreement with CO quantum yields obtained in other alkanes, alcohols, and acetonitrile.¹

(1) K. Gollnick and E. Leppin, *J. Amer. Chem. Soc.*, **92**, 2217 (1970).

(2) H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **4**, 143 (1966).

Table I. Experimental and Statistical Product Distributions and Relative Rates of S(¹D) Insertion Reactions into C-H Bonds

Alkanes	Mercaptans ^a		
	Primary	Secondary	Tertiary
(a) (b) CH ₃ CH ₂ CH ₂ CH ₂ CH ₃ <i>n</i> -Pentane	48 (50.0) <i>1.00</i>	(a) 33 (33.3) <i>1.03</i> (b) 19 (16.7) <i>1.19</i>	
CH ₃ (b) (a) CH ₃ CHCH ₂ CH ₃ Isopentane	(a) 16 (25.0) <i>1.00</i> (b) 47 (50.0) <i>1.47</i>	23 (16.7) <i>2.16</i>	14 (8.3) <i>2.64</i>
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃ <i>n</i> -Hexane	33 (42.8) <i>1.00</i>	67 ^b (57.2) <i>1.48</i>	
CH ₃ (b) (a) CH ₃ CH ₂ CHCH ₂ CH ₃ 3-Methylpentane	(a) 35 (42.8) <i>1.00</i> (b) 18 (21.4) <i>1.02</i>	<i>erythro:</i> 17.5 (14.3) <i>1.49</i> <i>threo:</i> 17.5 (14.3) <i>1.49</i>	12 (7.1) <i>2.06</i>
(b) CH ₃ (a) CH ₃ CCH ₂ CH ₃ CH ₃ 2,2-Dimethylbutane	(a) 14.5 (21.4) <i>1.00</i> (b) 66.5 (64.3) <i>1.51</i>	19.0 (14.3) <i>1.96</i>	
CH ₃ CH ₃ CHCHCH ₃ CH ₃ 2,3-Dimethylbutane	80 (85.7) <i>1.00</i>		20 (14.3) <i>1.50</i>
CH ₃ H ₂ C-CH-CH ₂ (a) H ₂ C-CH ₂ (b) CH ₂ (c) Methylcyclohexane	17.3 (21.4) <i>1.00</i>	(a) 15.6 (14.3) <i>cis</i> 16.7 (14.3) <i>trans</i> <i>1.45 trans</i> (b) 13.8 (14.3) <i>cis</i> 14.0 (14.3) <i>trans</i> <i>1.21</i> (c) 6.5 (7.2) <i>cis</i> 6.5 (7.2) <i>trans</i> <i>1.12</i>	9.6 (7.2) <i>1.65</i>

^a Experimental values in per cent (first numbers given), theoretical statistical product distribution in per cent (numbers in parentheses), relative rates (italic numbers) determined from the ratios of experimental values over theoretical statistical distribution values and normalized to the lowest relative rate. ^b The secondary mercaptans, 2- and 3-hexanethiol, could not be separated gas chromatographically.

guished by their characteristic retention behavior. Different primary or secondary mercaptans, however, are distinguished by assuming that in solution S(¹D) atoms react with C-H bonds at random (or at least approximately so), as is the case in the gaseous phase.² Identification by applying this assumption was proved to be correct in all cases where authentic samples were available.³

Table I summarizes the results. The experimental values are mean values from several experiments. The limits of error are estimated to be 1-2% absolute in case of the open-chain alkanethiols and certainly less than 1% absolute in case of methylcyclohexanethiols.

Whereas mercaptan formation occurs practically at random with *n*-pentane, the rate of S(¹D) atom reactions with C-H bonds of the other alkanes increases in the order primary < secondary < tertiary C-H bonds. If we consider the C-H bonds of methyl and methylene groups in CH₃-CH₂-CH₂R as "nonactivated," the C-H bonds of the methylene group are drastically (by 50-100%) activated if CH₂R groups are replaced by *sec*-butyl, isopropyl, or *t*-butyl groups. Similar effects are exerted on the reactivities of the primary and tertiary C-H bonds by replacing neighboring CH₂CH₂R groups

by higher branched alkyl groups or by a methyl group. Thus, the comparatively low value of 1.5 for the relative reactivity of the tertiary C-H bonds in 2,3-dimethylbutane toward reactions with S(¹D) atoms does not indicate a sterically hindered reaction but rather an enhanced reactivity of the primary C-H bonds of this compound.

The selectivity of S(¹D) atom reactions in solution contrasts sharply with the nonselective reactions of singlet D sulfur atoms in the gas phase.

We have already noticed that, with regard to the competing reactions 2 and 3, reaction 2 is favored over reaction 3 more strongly in the gas phase than in solution.¹ This was considered to be due to a loss of excess translational energy of S(¹D) atoms in solution as compared with those in the gas phase. Obviously, this assumption holds also for explaining the selectivity of S(¹D) atom reactions in solution.

The C-O equilibrium distances in carbonyl sulfide (1.16 Å) and in carbon monoxide (1.13 Å) are nearly the same. The C-O stretching vibration is apparently not excited in electronically excited COS as was deduced from its absorption spectrum.⁶ Therefore, it is per-

(6) E. Leppin and K. Gollnick, *Mol. Photochem.*, in press.

missible to assume that all the excess energy released in the dissociation process of electronically excited COS is distributed among the dissociation products, CO and S(¹D), only as translational energy according to the masses of the fragments.⁷ Since the dissociation process requires about 100 kcal/mol,² about 25 or 12 kcal/mol of excess energy is available if COS is photolyzed in the gas phase at 2288 Å (Cd resonance lamp) or at 2537 Å, respectively, thus leaving about 13 or 6 kcal/g-atom of excess translational energy, respectively, to the S(¹D) atom. However, if the photolysis takes place in solution, COS, excited at 2537 Å into the third vibrational level of its ¹Δ or ¹Σ⁻ state,⁶ may be deactivated to the corresponding zero vibrational state before predissociation occurs, thus leaving less than 3 kcal/g-atom excess translational energy to the S(¹D) atoms.

In the gas phase, less than 5 kcal/mol of activation energy is required for S(¹D) atom reactions with C-H bonds.⁸ S(¹D) atoms having about 13 or 6 kcal/g-atom initial excess translational energy give rise to statistical mercaptan formation; however, the rates of reactions increase with increasing initial excess translational energies.⁸ Therefore, the statistical mercaptan formation in the gas phase is likely to result from reactions of S(¹D) atoms that are *not thermalized* when they react with C-H bonds. This is supported by the fact that singlet methylene, ¹CH₂, generated by photolysis of diazomethane, does give rise to selectivity in its gas-phase reactions with C-H bonds,⁹ although these processes are more exothermic than the corresponding reactions with S(¹D) atoms.¹⁰ In other words, if the S(¹D) atoms were thermalized, an even higher selectivity in its reactions with C-H bonds should be observed than that obtained with singlet methylene.

The selectivity of the S(¹D) atom reactions in solution should, therefore, be due to reactions of *thermalized* S(¹D) atoms rather than to slight complexing of these atoms with solvent molecules during the mercaptan-forming reactions.

Whereas S(¹D) atoms were found to react with C-H bonds selectively in the liquid phase and nonselectively in the gas phase, chlorine atoms^{16,17} and singlet methylene^{14,18-20} react more selectively in the gas phase than in the liquid phase.²¹

(7) Compare, e.g., R. C. Mitchell and J. P. Simons, *Discuss. Faraday Soc.*, **44**, 208 (1967).

(8) O. P. Strausz in "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience Publishers, New York, N. Y., 1967, Chapter 2.

(9) H. M. Frey, *J. Amer. Chem. Soc.*, **80**, 5005 (1958).

(10) The enthalpies of formation of ¹CH₂ and S(¹D) are 95 kcal/mol^{11,12} and 93 kcal/g-atom,¹³ respectively. Thus the exothermicity of their reactions are about 100 and 85-90 kcal/mol,⁸ respectively.

(11) G. v. Bünau, P. Potzinger, and G. O. Schenck, *Tetrahedron*, **21**, 1293 (1965).

(12) The enthalpy of formation of ³CH₂ was determined to be 85 kcal/mol,¹¹ in agreement with a value of 80-86 kcal/mol estimated by others.¹⁴

(13) Calculated from ΔH_f(S(³P)) = 66.7 kcal/g-atom¹⁵ and an energy of the electronically excited sulfur D atom of 26.40 kcal/g-atom.

(14) W. B. DeMoore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).

(15) S. W. Benson, "Thermochemical Kinetics," John Wiley and Sons, Inc., New York, N. Y., 1967, Appendix, Table A.8.

(16) F. R. Mayo, *J. Amer. Chem. Soc.*, **89**, 2654 (1967), and literature cited.

(17) J. M. Tedder, *Quart. Rev. (London)*, **14**, 336 (1960).

(18) J. A. Bell, *Progr. Phys. Org. Chem.*, **2**, 1 (1964).

(19) H. M. Frey in "Progress in Reaction Kinetics," Vol. 2, G. Porter, Ed., Pergamon Press, Oxford, England, 1964, p 131.

(20) W. Kirmse, H. M. Frey, P. P. Gaspar, and G. S. Hammond, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

(21) In solution, singlet methylene has been reported to react completely at random with C-H bonds of a large series of alkanes.²²⁻²⁴

For chlorine atoms, the loss of selectivity on change from the gas-phase to liquid-phase reactions is explained as resulting from the great reactivity of chlorine atoms in solution, so that a chlorine atom caged in by the solvent will be held at a particular site long enough for there to be a high probability of reaction even though there are more reactive sites elsewhere.¹⁷ Mayo¹⁶ concluded that the chlorine atom in solution is so reactive and its lifetime is so short that its reactions depend on the statistics of a series of cage encounters ("cage effect") as well as on the relative reactivities of the surrounding carbon-hydrogen bonds involved; it should follow that this liquid-phase-gas-phase difference will disappear as the attacking radicals become less reactive and their lifetimes become long compared with the times required for diffusion. Frey²⁰ reported that the rates of singlet methylene reactions with C-H bonds in the gas phase are close to collision frequencies, and in solution, reactions with primary, secondary, and tertiary C-H bonds occur with very similar, temperature-independent rate constants,^{19,22-24} indicating that ¹CH₂ reactions with C-H bonds in solution are close to being diffusion controlled.

S(¹D) reactions with C-H bonds in the gas phase, initiated by photolysis of COS at 2537 Å, are very probably far from being close to collision frequencies. A lower limit of $5 \times 10^7 M^{-1} \text{sec}^{-1}$ has been estimated,^{8,27} whereas the same value was found to be an upper limit in liquid-phase reactions (see below). Comparing ¹CH₂ and S(¹D) atom reactions in solution, the decrease of reactivity is accompanied by an increase in selectivity as expected.

The maximum selectivity that could be achieved so far for ¹CH₂ reactions in the gas phase with primary,

However, recently the reactions of ¹CH₂ with the primary, secondary, and tertiary C-H bonds of isopentane were found to occur with relative rates of 1.00:1.22:1.51 in solution and of 1.00:1.22:1.39 in the gas phase.²⁵ Since the ratio found for the gas-phase reaction was independent of the photolyzing wavelength, it was concluded that excess translational energy of methylene has no effect on its reactivity and that, therefore, singlet methylene is translationally thermalized before it reacts with C-H bonds. The small increase in selectivity which is observed for the reaction of methylene with the tertiary C-H bond of isopentane in solution as compared to the corresponding reaction in the gas phase, is assumed to be due to participation of triplet methylene, ³CH₂, in the liquid-phase reaction.²⁵ ³CH₂ reacts in hydrogen abstraction reactions more selectively than does ¹CH₂ in insertion reactions,²³⁻²⁶ and some authors^{23,24,26} infer that any selectivity that is observed for methylene insertion reactions in solution is due to ³CH₂ reactions exclusively. A similar explanation is, however, not applicable to sulfur atom reactions, since neither in the gas phase nor in the liquid phase, are S(³P) atoms capable of mercaptan-forming reactions with C-H bonds.

(22) W. v. E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Amer. Chem. Soc.*, **78**, 3224 (1956).

(23) D. B. Richardson, M. S. Simmons, and I. Dvoretzky, *ibid.*, **82**, 5001 (1960).

(24) D. B. Richardson, M. C. Simmons, and I. Dvoretzky, *ibid.*, **83**, 1934 (1961).

(25) B. M. Herzog and R. W. Carr, Jr., *J. Phys. Chem.*, **71**, 2688 (1967).

(26) G. Z. Whitten and B. S. Rabinovitch, *ibid.*, **69**, 4348 (1965).

(27) Quite recently, COS was photolyzed in the gas phase at 1440-1570 Å and the rate constant for the process S(¹D) + COS → S₂ + CO was estimated to be $4 \times 10^{10} M^{-1} \text{sec}^{-1}$ or greater.^{28,29} From the relative rates of this reaction and the reaction of S(¹D) atoms with C-H bonds,² the rate constant for the latter process would be about $2 \times 10^{10} M^{-1} \text{sec}^{-1}$ or greater; i.e., the reactions would proceed with rates close to collision frequencies. This is understandable since the S(¹D) atoms produced in the far-ultraviolet may be extremely "hot" when they react, because their initial excess translational energy may become as great as about 40 kcal/g-atom if all excess energy at 1570 Å is transformed into translational energy of CO and S(¹D).

(28) R. J. Donovan, *Trans. Faraday Soc.*, **65**, 1419 (1969).

(29) R. J. Donovan, L. J. Kirsch, and D. Husain, *Nature*, **222**, 1164 (1969).

Table II. $f_r(R)$ Values of Different Hydrogen Atoms in Alkanes^a and Relative Rates^b of S(¹D) Insertions into the Corresponding C-H Bonds

Alkanes	Hydrogens			
	Primary		Secondary	Tertiary
(a) (b) CH ₃ CH ₂ CH ₂ CH ₂ CH ₃ <i>n</i> -Pentane	0.0240	<i>1.00</i>	(a) 0.0475 (b) 0.0587	<i>1.03</i> <i>1.19</i>
(b) CH ₃ CH ₃ CHCH ₂ CH ₃ Isopentane	(a) 0.0278 (b) 0.0286	<i>1.00</i> <i>1.47</i>	0.0481	2.16 0.0745 2.64
(b) CH ₃ CH ₃ CH ₂ CHCH ₂ CH ₃ 3-Methylpentane	(a) 0.0187 (b) 0.0204	<i>1.00</i> <i>1.02</i>	0.0390	1.49 0.0683 2.06

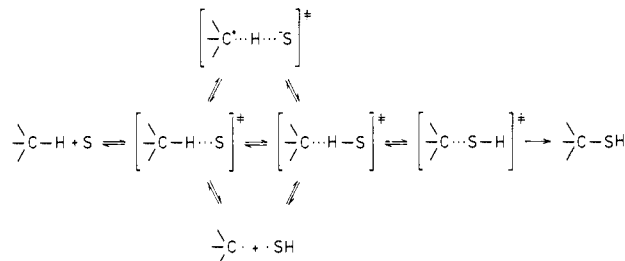
^a After Fukui.³² ^b Italic numbers.

secondary, and tertiary C-H bonds is about 1.0:1.2:1.5;^{19,20} for S(¹D) atoms in solution it is about 1.0:2.2:2.6. The enhanced selectivity in S(¹D) atom reactions may be explained on the basis of Hammond's postulate³⁰ in that, since S(¹D) atom reactions with C-H bonds are less exothermic than the corresponding reactions with ¹CH₂ by 10–15 kcal/mol, more C-H bond stretching is expected to occur in the transition state with S(¹D) than with ¹CH₂, thus resulting in enhanced discrimination among the various C-H bonds of different bond strength.

With regard to the mechanism of the mercaptan-forming process 2, the reaction of S(¹D) atoms with C-H bonds in the gas phase is considered as occurring as a concerted, single-step insertion-type process.⁸ The absence of products such as H₂S, H₂S₂, and products expected from alkyl radical recombination reactions when COS is photolyzed in alkane solutions also favors a mechanism according to which S(¹D) atom reactions with C-H bonds proceed in a concerted fashion, especially since these reactions occur with retention of configuration (see next paragraph).

For the gas-phase reactions as well as for the liquid-phase reactions, little is known about the transition states involved in the concerted reactions. A three-membered cyclic transition state to be involved in S(¹D) atom reactions with C-H bonds explains nicely the observed stereospecificity of these reactions and probably represents the ideal model for what is called an "insertion" reaction. However, a process involving a three-membered transition state seems to be structurally very unlikely, as was discussed by Benson³¹ for the insertion reactions of ¹CH₂, in that fairly bulky species such as ¹CH₂ can hardly attack the electrons on the compact C-H bonds, since these processes should occur with very small frequency factors and fairly high activation energies, contrary to experimental results. DeMoore and Benson¹⁴ favor, therefore, a process in which ¹CH₂ attacks the H atom of the C-H bond initially, thus forming a transition state in which the two radicals produced are essentially H-bonded; rotation of the radical pair into favorable positions for C-C bond formation then occurs before separation takes place. The attractive potential between the loosely associated radicals is ascribed to partial contribution of ionic states.

This mechanism, which has been extended to gas-phase S(¹D) atom reactions with C-H bonds² and favored over the three-center mechanism because it explains the high reactivity of S(¹D) atoms toward the protonic C-H bonds and the even higher reactivity toward the hydridic Si-H bonds,⁸ seems to be especially attractive for S(¹D) insertion reactions in solution, in which the solvent cage may represent an additional force that prevents the radical pair from separation. It explains the increasing reactivity of primary < secondary < tertiary C-H bonds toward S(¹D) atoms since, in this order, the C-H bond dissociation energies decrease, whereas the stabilities of the alkyl radicals (as well as of the carbonium ions in the contributing ionic states, S⁻...H...R⁺) increase.



An additional support in favor of the Benson mechanism for the S(¹D) insertion reaction is the finding that the rates of S(¹D) atom reactions with C-H bonds in solution parallel the $f_r(R)$ indices calculated by Fukui,³² which represent intramolecular measures of the frontier electron densities at the hydrogen atoms of a particular hydrocarbon. In Table II, $f_r(R)$ values are compared to the relative rates determined for S(¹D) atom reactions with *n*-pentane, isopentane, and 3-methylpentane (for the other hydrocarbons of Table I, no $f_r(R)$ values are available).

(b) Stereospecificity of Singlet D Sulfur Atom Insertion Reactions

The absence of products like H₂S, H₂S₂, and alkyl radical recombination products as well as the formation of *erythro*- and *threo*-2-mercapto-3-methylpentane from 3-methylpentane in a 1:1 ratio strongly indicate that free radicals are not involved in the S(¹D) insertion reactions.³³

(30) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(31) S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964).

(32) K. Fukui in "Modern Quantum Chemistry," O. Sinanoğlu, Ed., Academic Press, New York, N. Y., 1965, Istanbul Lectures, Part 1: Orbitals, p 49.

A further experimental support for this view is found in the fact that S(¹D) atom reactions with *trans*- and *cis*-1,4-dimethylcyclohexane give rise to tertiary mercaptans, in which the geometry of the methyl groups is retained.

Photolysis of COS in *trans*-1,4-dimethylcyclohexane (**1a**) and *cis*-1,4-dimethylcyclohexane (**1b**) at 2537 Å resulted in the formation of a mixture of mercaptans that were separated by gas chromatography. The components of the mixtures were identified as follows (compare ref 3). Consider the mixture of mercaptans formed from **1a** (Figure 1). First of all, one expects one primary mercaptan (**5a**), two secondary mercaptans (**3a**, **4a**), and either one (**2a**) or two tertiary mercaptans (**2a**, **2b**), depending on whether the S(¹D) atom reaction occurs as insertion or *via* a mechanism which involves the production of free radicals. From the characteristic retention behavior of primary, secondary, and tertiary mercaptans it is unequivocally concluded that peak 2a must represent a tertiary, peaks 3a and 4a secondary, and peak 5a a primary mercaptan. The same characteristic pattern is found for the mixture of mercaptans from **1b**.

Since all possible mercaptans show clearly distinct retention times (Figure 1), it is undoubtedly demonstrated that from each dimethylcyclohexane only one tertiary mercaptan is formed and that these two tertiary mercaptans differ one from another. Using nonpolar capillary columns, the separation should occur according to the boiling points of the mercaptans in that those having higher boiling points should also have higher retention times. Since the change in free enthalpy is greater for the transformation of an equatorial methyl group into an axial methyl group than for the corresponding transformation of a SH group,³⁴ **2a** should have a lower boiling point and, consequently, a lower retention time than **2b**.³⁵ This shows then that the tertiary mercaptan formed from **1a** is indeed **2a** and that from **1b** is indeed **2b**, thus confirming our expectation that, if only one tertiary mercaptan is formed from each of the dimethylcyclohexanes, reactions of S(¹D) atoms with C-H bonds do proceed with retention of configuration rather than with inversion. Consequently, S(¹D) atom reactions with C-H bonds occur as insertion reactions provided that a tertiary radical, if formed from the dimethylcyclohexanes, is conformationally unstable. That this is the case has recently been shown for the tertiary radicals derived from the 1,2-dimethylcyclohexanes.³⁶

Stereospecificity is also observed with *cis*- and *trans*-1,2-dimethylcyclopropane. However, about 5% of the

(33) Abstraction of a secondary hydrogen by a halogen atom from 2-halogenobutanes yields *erythro*- and *threo*-2,3-dihalogenobutanes in about 7:3 ratios.¹⁷ This is explained by assuming that the 2-halogeno-1-methylpropyl radicals react in conformations that allow the incoming halogen molecule to attack the radical site in an easier manner on the side of the radical away from the substituent halogen. Similar deviations from a 1:1 ratio should be expected if 1,2-dimethylbutyl radicals were involved in the S(¹D) atom reaction with 3-methylpentane.

(34) J. A. Hirsch in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, N. Y., 1967, p 199.

(35) It follows that that of the secondary mercaptans, **3a** and **3b** must have lower retention times than **4a** and **4b**, respectively. Furthermore, it is seen from Figure 1 that **4b** and **5b** are produced from **1b** to a smaller extent than are **4a** and **5a** from **1a**. This is obviously due to steric 1,3 hindering exerted by the axial CH₃ group and the axial H atoms that are *cis* to this methyl group in **1b** toward the incoming S(¹D) atom.

(36) A. G. Anastassiou and H. E. S. Simmons, *J. Amer. Chem. Soc.*, **89**, 3177 (1967).

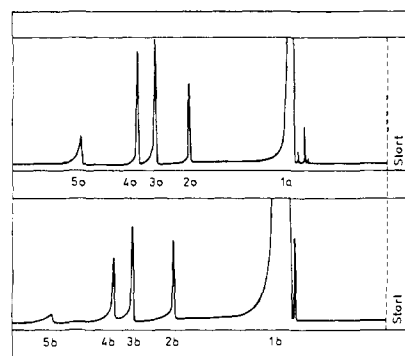
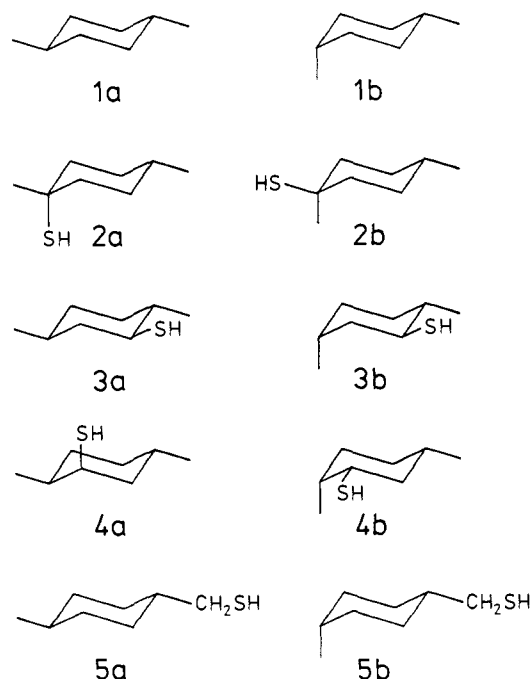


Figure 1. Gas chromatogram of thiols from *trans*-1,4-dimethylcyclohexane (**1a**) and from *cis*-1,4-dimethylcyclohexane (**1b**).



“wrong” tertiary mercaptan is formed in each case. Whether this is due to isomerization of some of the initially formed “correct” mercaptans because of having some excess energy, or to the formation of some conformationally unstable tertiary free radicals, remains unknown. No isomerization of the starting hydrocarbons during the COS photolysis occurred, however, that might explain the production of the “wrong” isomers.

(c) Deactivation of Singlet D Sulfur Atoms to Triplet P Sulfur Atoms by Solvent Molecules

In the preceding paper¹ we have pointed out that only a small fraction of the triplet P sulfur atoms formed during direct photolysis of COS in alkanes, alcohols, and acetonitrile can result from dissociation of excited triplet COS. Thus, most of the S(³P) atoms are generated from S(¹D) atoms by interaction with solvent molecules (reaction 3). Similar results are obtained when COS photolyses are carried out in and are sensitized by aromatic hydrocarbons such as benzene, toluene, and *p*-xylene.³⁷

The formation of S(³P) atoms in alcoholic solution, in acetonitrile, and in aromatic hydrocarbons can easily be demonstrated by trapping them quantitatively in the

(37) E. Leppin and K. Gollnick, publication in preparation.

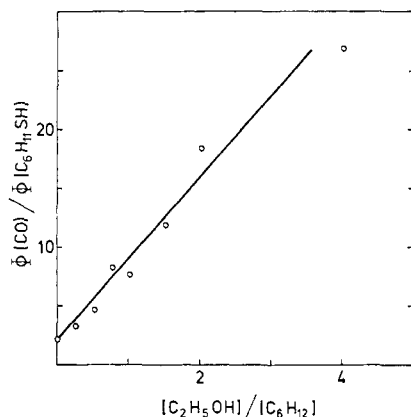


Figure 2. Ratio of quantum yields $\Phi(\text{CO})/\Phi(\text{C}_6\text{H}_{11}\text{SH})$ as a function of the ratios of concentrations of ethyl alcohol and cyclohexane.

presence of relatively small quantities of the very reactive 2,3-dimethyl-2-butene as episulfide (tetramethylthiirane),^{37,38} Under these conditions episulfide production from $\text{S}(^1\text{D})$ atom reactions with the olefin can be excluded. This is inferred from the fact that higher amounts of alkanes must be added to alcoholic and aromatic hydrocarbon solutions in order to trap the $\text{S}(^1\text{D})$ atoms by their insertion reactions. Quantitatively, photolyses of COS in mixtures of an alkane such as cyclohexane and an alcohol, e.g., ethyl alcohol, can be used to determine relative rate constants for $\text{S}(^1\text{D})$ insertion and $\text{S}(^1\text{D})$ deactivation reactions.

According to reaction 2 (with $k_2^{\text{C}_6\text{H}_{12}}$ for $\text{S}(^1\text{D})$ insertion into the C-H bonds of cyclohexane) and reaction 3 (with $k_3^{\text{C}_6\text{H}_{12}}$ and k_3^{EtOH} for deactivation of $\text{S}(^1\text{D})$ atoms by cyclohexane and ethyl alcohol, respectively)

$$\Phi(\text{CO})/\Phi(\text{C}_6\text{H}_{11}\text{SH}) = 1 + k_3^{\text{C}_6\text{H}_{12}}/k_2^{\text{C}_6\text{H}_{12}} + k_3^{\text{EtOH}}[\text{EtOH}]/k_2^{\text{C}_6\text{H}_{12}}[\text{C}_6\text{H}_{12}] \quad (4)$$

where $\Phi(\text{CO})$ and $\Phi(\text{C}_6\text{H}_{11}\text{SH}) =$ quantum yields of CO and cyclohexanethiol formation, respectively, since

$$d[\text{C}_6\text{H}_{11}\text{SH}]/dt = k_2^{\text{C}_6\text{H}_{12}}[\text{S}(^1\text{D})][\text{C}_6\text{H}_{12}] \quad (5)$$

$$d[\text{S}(^1\text{D})]/dt = (I)\Phi(\text{CO}) - [(k_2^{\text{C}_6\text{H}_{12}} + k_3^{\text{C}_6\text{H}_{12}})[\text{C}_6\text{H}_{12}] + k_3^{\text{EtOH}}[\text{EtOH}]][\text{S}(^1\text{D})] = 0 \quad (6)$$

where $I =$ number of light quanta absorbed per unit time by COS) and

$$d[\text{C}_6\text{H}_{11}\text{SH}]/I dt = \Phi(\text{C}_6\text{H}_{11}\text{SH}) \quad (7)$$

Plotting $\Phi(\text{CO})/\Phi(\text{C}_6\text{H}_{11}\text{SH})$ vs. $[\text{EtOH}]/[\text{C}_6\text{H}_{12}]$ (Figure 2), the ratios of rate constants, determined from the slope and from the intercept of the straight line with the ordinate, are found to be $k_3^{\text{EtOH}}/k_2^{\text{C}_6\text{H}_{12}} = 7$ and $k_3^{\text{C}_6\text{H}_{12}}/k_2^{\text{C}_6\text{H}_{12}} = 1$, respectively. Using benzene as solvent in the benzene-sensitized COS photolysis,³⁷ $k_3^{\text{benzene}}/k_2^{\text{C}_6\text{H}_{12}} = 200$. Thus

$$k_2^{\text{C}_6\text{H}_{12}} : k_3^{\text{C}_6\text{H}_{12}} : k_3^{\text{EtOH}} : k_3^{\text{benzene}} = 1 : 1 : 7 : 200 \quad (8)$$

(38) Attempts to trap $\text{S}(^3\text{P})$ atoms in alkane solution in the presence of olefins result in the formation of mixtures of mercaptans (from $\text{S}(^1\text{D})$ insertion reactions into the alkanes) and of sulfides and disulfides (from mercaptan photolysis and subsequent thyl radical reactions with olefins and alkanes).³⁹

(39) E. Leppin and K. Gollnick, *Chem. Ber.*, in press.

showing that the $\text{S}(^1\text{D}) \rightarrow \text{S}(^3\text{P})$ transition is enhanced by about one or two orders of magnitude when alcohols or aromatic hydrocarbons are applied as solvents, respectively, instead of saturated hydrocarbons. Assuming that benzene deactivates $\text{S}(^1\text{D})$ atoms in a diffusion-controlled process, i.e., $k_3^{\text{benzene}} \approx 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$, an upper limit for the rate constant of the $\text{S}(^1\text{D})$ insertion reaction into the C-H bonds of cyclohexane can be obtained as $k_2^{\text{C}_6\text{H}_{12}} \approx 5 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$.

With regard to the mechanism of the deactivation reaction, one has to consider the various pathways available for the dissipation of the electronic energy of $\text{S}(^1\text{D})$ atoms that is released during the $\text{S}(^1\text{D}) \rightarrow \text{S}(^3\text{P})$ transition. Of these pathways, energy transfer from $\text{S}(^1\text{D})$ atoms to solvent molecules producing electronically excited solvent molecules is excluded since the lowest electronically excited states of the solvents used are located at much higher energy levels above their ground states than 26.4 kcal/mol. Furthermore, conversion of electronic energy by inelastic collisions into translational or vibrational energy of the collision partner is a very improbable process⁴⁰⁻⁴² and is thus also excluded from further consideration. However, if *chemical interaction* takes place between an electronically excited species and a ground-state molecule, electronic excitation energy of the energy-donating species may be transformed into vibrational energy of the energy-accepting molecule *via* an internal conversion or intersystem-crossing process in the intermediate quasi-molecule formed by that chemical interaction. A classical example for this kind of energy dissipation mechanism is that of the quenching of fluorescence of $\text{Na}(^2\text{P})$ atoms by saturated and unsaturated hydrocarbons.⁴³ Recently, quenching of fluorescence of aromatic hydrocarbons by 1,3-dienes⁴⁴ in solution, quenching of fluorescence of naphthalene by sulfoxides in solution,⁴⁵ and quenching of excited mercury atoms, $\text{Hg}(^3\text{P}_1)$, by various substrates in the gas phase⁴⁶⁻⁴⁸ have been explained as occurring *via* such electronically excited complexes.

With respect to the nature of the chemical interaction, electron transfer has been proposed by Weiss⁴⁹ as early as 1939, and recently electron donor-acceptor complexes (EDA complexes)⁵⁰ were spectroscopically identified as intermediates produced by interactions of electronically excited species and ground-state molecules.⁵¹⁻⁵⁴ Perhaps excited EDA complexes may pro-

(40) A. B. Callear in "Photochemistry and Reaction Kinetics," P. G. Ashmore, F. S. Dainton, and T. M. Sudgen, Ed., University Press, Cambridge, 1967, p 133.

(41) T. L. Cottrell, "Dynamic Aspects of Molecular Energy States," Oliver and Boyd, Edinburgh, 1965.

(42) P. G. Dickens, J. W. Linnet, and O. Sovers, *Discuss. Faraday Soc.*, 33, 52 (1962).

(43) K. J. Laidler, "The Chemical Kinetics of Excited States," Clarendon Press, Oxford, 1955.

(44) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, 88, 3665, 3893 (1966).

(45) R. S. Cooke and G. S. Hammond, *ibid.*, 90, 2958 (1968).

(46) H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, 1, 209 (1963).

(47) E. Jakubowski, P. Kebarle, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, 45, 2287 (1967).

(48) M. D. Scheer and J. Fine, *J. Chem. Phys.*, 36, 1264 (1962).

(49) (a) J. J. Weiss, *Trans. Faraday Soc.*, 35, 48 (1939); (b) J. J. Weiss in "The Chemistry of Ionization and Excitation," Proceedings of a Conference on Radiation Chemistry and Photochemistry, Newcastle upon Tyne, 1966, G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, London, 1967, p 17, and literature cited.

(50) G. Briegleb, "Electronen-Donator-Akzeptor-Komplexe," Springer-Verlag, Berlin, 1961.

(51) H. Beens and A. Weller, *Chem. Phys. Lett.*, 2, 140 (1968).

(52) A. Weller, *Pure Appl. Chem.*, 16, 115 (1968).

vide for one of the most important pathways of radiationless transitions in electronically excited molecules. EDA complexes should occur preferentially in the condensed phase since charge separation should be favored by solvation of the ionic states thus formed.

The direction of electron transfer depends on the ionization potentials and electron affinities of the partners in that the molecule with the lower ionization potential and the lower electron affinity serves as the electron donor. Since the electron affinity of molecules (and atoms) in electronically excited states is increased by the amount of their excitation energies,⁵⁵ electronically excited molecules or atoms quite often serve as electron acceptors in EDA complexes. This is certainly the case when $S(^1D)$ atoms form EDA complexes with solvent molecules since their electron affinity should exceed 3 eV (2.1 eV electron affinity of $S(^3P)$ ⁵⁶ + 1.1 eV excitation energy), thus surpassing the strongest ground-state electron acceptors such as tetracyanoethylene (1.6 eV), chloranil (1.35 eV), or iodine molecule (0.8 eV).⁵⁰ We may, therefore, expect that $S(^1D)$ atoms in solution give rise to the formation of EDA complexes, the interactions of which increase with the electron-donating properties of the solvent molecules in the order saturated hydrocarbons, alcohols, aromatic hydrocarbons.

A simple potential energy curve diagram for EDA complexes between an electron donor D and the electron acceptors $S(^1D)$ and $S(^3P)$ is shown in Figure 3. The binding energy between $S(^1D)$ and D in the complex \tilde{A} should be enhanced as compared with that of

(53) S. Ander, H. Blume, G. Heinrich, and D. Schulte-Frohlinde, *Chem. Commun.*, 745 (1968).

(54) D. Schulte-Frohlinde and R. Pfefferkorn, *Ber. Bunsenges. Phys. Chem.*, 72, 330 (1968).

(55) H. Leonhard and A. Weller, *ibid.*, 67, 791 (1963).

(56) B. L. Moiseiwitsch in "Advances in Atomic and Molecular Physics," Vol. 1, D. R. Bates and I. Estermann, Ed., Academic Press, New York, N. Y., 1965, p 61.

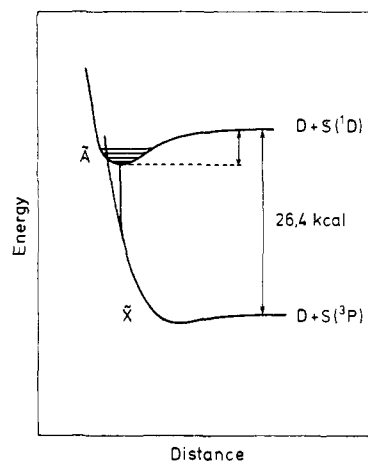


Figure 3. Potential energy curve diagram for EDA complexes of an electron donor D and the electron acceptors $S(^1D)$ and $S(^3P)$.

$S(^3P)$ and $D(\text{complex } \tilde{X})$ and is estimated to be of the order of a few kilocalories per mole by comparison with ordinary EDA complexes such as trinitrobenzene-naphthalene. When $S(^1D)$ approaches D, electronic energy of $S(^1D)$ corresponding to the amount of this binding energy is transformed into vibrational energy of the complex \tilde{A} , which in turn is transformed into translational energy of the surrounding solvent molecules. From the zero vibrational level of \tilde{A} , transition to the ground-state complex \tilde{X} may occur either by emission (phosphorescence in the infrared) or by intersystem crossing, thus transforming the residual electronic energy into translational energy of the fragments, $S(^3P)$ and D, if \tilde{X} is a more or less repulsive state, as indicated in Figure 3. Further experiments directed toward the elucidation of the deactivation process of $S(^1D)$ atoms by various ground-state molecules are under way.